Abstract

Cu/ZnO catalysis, prepared in an automated synthesis by coprecipitation, were tested for methanol synthesis by high throughput screening using a 49-channel parallel flow reactor. The activity strongly depends on the preparation conditions and the calcination temperature. Interesting samples were selected for deeper characterization by EXAFS including in situ spectroscopic studies during temperature programmed reduction. Both ageing time and calcination temperature had a strong influence on the reduction behaviour of CuO/ZnO samples and thus resulted in an altered catalytic activity. In all cases, only a small fraction of Cu(I) species was formed during reduction.

1. Introduction

X-ray absorption spectroscopy is known to be a powerful technique in catalysis research. It does not only provide structural information on the crystalline phases but also gives (element-specific) information on the amorphous part of the catalyst [1–5]. In addition, structural transformations of solid catalysts both in gaseous or liquid reaction environment can be studied in situ and in a time-resolved manner [4–7], which allows to establish structure-activity relationships.

High-throughput experimentation (HTE)-technology for the preparation of heterogeneous catalysts using synthesis robots and multichannel parallel flow reactor systems has emerged as a powerful tool in catalysis research in recent time [8–11]. The method is effective to screen catalysts with respect to composition or preparation parameters.

Although a number of materials can be produced and tested using both synthesis robots and parallel reactor technology, this approach cannot substitute a rational design of catalysts, considering that the number of materials to be prepared is principally unlimited. Therefore, a combination of both approaches seems most promising. A structural characterization of all samples tested would be extremely time-consuming. More efficient is the selection of samples with distinct properties, as indicated from pre-characterization and catalytic tests for gaining structure-activity relationships. In this contribution, we illustrate how the EXAFS technique can contribute to this strategy.

For this purpose, the Cu/ZnO system is a well-suited example. During the past years it has been thoroughly investigated [12–19], also with respect to preparation parameters (composition, pH dependence of precipitation, calcination temperature, ageing). In particular, calcination and ageing seem to play a crucial role. Testing of the catalyst samples usually takes about one week considering the activation and equilibration time and thus parallel testing is advantageous. The future role of EXAFS in this area is discussed in this contribution.

2. Experimental

2.1. Catalyst preparation and testing

Automated synthesis and a 49-fold parallel reactor system, applicable at elevated pressure (50 bar), were used for the preparation of the samples and for activation/catalytic testing in methanol synthesis, respectively. The principal procedure is shown in Figure 1. Catalysts were precipitated at constant pH. During ageing, the pH just recorded and samples were taken from the suspension at certain times. More detailed information on the preparation procedure and the catalyst testing conditions can be found in ref. [20]. The prepared samples were characterized by X-ray diffraction, thermal analysis, and for selected reactive frontal chromatography was used to determine the copper surface area.

2.2. X-ray absorption spectroscopy

Reduction of the Cu/ZnO samples is an important feature in the understanding of the catalytic performance of the catalysts, which can be monitored with respect to Cu(II), Cu(I) and Cu(0)-species with X-ray absorption near edge structure. The XAS experiments were performed at beamline BM1B (Swiss-Norwegian Beamline) at ESRF (Grenoble, France) and at ANKA-XAS (Karlsruhe, Germany) in a reactor for pellet-shaped samples. Pellets with diameter of 13 mm and thickness of 1.5 mm were pressed from finely ground catalyst diluted with boron nitride and loaded in an in situ reactor cell with X-ray transparent windows and oven. The XAS data were obtained in transmission geometry using a Si(111) monochromator in both cases and EXAFS and XANES data were taken around the Cu K-edge (8.979 keV). The fraction of Cu(II), Cu(I)

Fig. 1. Synthesis procedure of Cu/ZnO catalysts used in high throughput screening activity tests at 50 bar (picture depicts 49-fold high throughput reactor)
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